

***ARRHENIUS TEMPERATURE DEPENDENCE OF HOMOGENEOUS
NUCLEATION RATES***

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(Extended Abstract)

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Arrhenius Temperature Dependence of Homogeneous Nucleation Rates

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Abstract. A simple yet physically-based and highly accurate parameterization of the nucleation rate is obtained. In essence, the log nucleation rate is expanded in special coordinates suggested by the first and second nucleation theorems and only linear terms are retained. The results support an Arrhenius model of the temperature dependence and are highly accurate over the range of a typical set of measurements – about 3-5 orders of magnitude in nucleation rate. This range is likely sufficient for most applications to atmospheric particle formation, which now seem feasible without need for bulk properties estimation, as would be required using classical nucleation theory, and without significant higher-order corrections to the linear result.

Key Words: Homogeneous nucleation; Nucleation theorem; Arrhenius temperature dependence

The present study is an outgrowth of two new papers that combine nucleation theorems and multivariate analysis to obtain a simple parameterization of nucleation rate – one both physically based and highly accurate [1,2]. In essence, the log nucleation rate is expanded in special coordinates suggested by the first and second nucleation theorems with only linear terms retained. For the most general result, homogeneous nucleation in a multi-component vapor system, the result is:

$$\ln J \approx \ln J_0 + \sum_i (g_i^* + \delta_i)(\ln n_i - \ln n_i^0) - \frac{\Delta E(g_1^*, g_2^*, \dots)}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right). \quad (1)$$

J ($cm^{-3}s^{-1}$) is nucleation rate, k is Boltzmann's constant, T is temperature ($^{\circ}K$), and n_i (cm^{-3}) is the vapor concentration of species i . The label “0” refers to the center of expansion - a reference condition conveniently set by the centroid of the experimental data expressed in nucleation-theorem motivated coordinates, $\{\ln J, \{\ln n_i\}, 1/T\}$, with $n+1$ coordinates for an n -component mixture and temperature dependence. The coefficients in Eq. 1 are readily obtained by applying standard multi-linear regression to a set of rate measurements. Especially noteworthy is that these coefficients have direct physical significance: g_i^* is the number of molecules of species i present in the critical nucleus, δ_i is a small kinetic term (its value is between 0 and 1) related to the direction of nucleation flux over the free energy surface. $\Delta E(g_1^*, g_2^*, \dots)$ is the energy of critical cluster formation from its *vapor-phase* components. Equivalent to Eq. 1:

$$J = J_0 \prod_i \left(\frac{n_i}{n_i^0} \right)^{g_i^* + \delta_i} \text{Exp} \left[- \frac{\Delta E(g_1^*, g_2^*, \dots)}{k} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (2)$$

showing the Arrhenius temperature dependence. The latter follows in principle from the second nucleation theorem expressed here in the less conventional form:

$$\left(\frac{\partial \ln J}{\partial T} \right)_{n_1, n_2, \dots} = \frac{\Delta E(g_1^*, g_2^*, \dots)}{kT^2} \quad (3)$$

whereby the concentrations of vapor species are held constant in taking the partial derivative [2]. In the more conventional form of the second nucleation theorem the saturation ratio is held constant – and the energy difference appearing on the right side is replaced by the difference between the critical cluster energy and that of the same number of molecules of bulk liquid (see Eq. 5 below).

In the absence of comprehensive multi-component nucleation rate measurements spanning a significant range of both temperature and vapor composition coordinates, Eqs. 1 and 2 were tested using reported measurements from several different sources. These included aerosol chamber measurements of nucleation rate in ternary organic acid/sulfuric acid/water systems at constant temperature [3], and nucleation pulse chamber measurements varying both temperature and vapor concentration for several single component vapor systems including water [4], methanol and n-hexanol [5], and nonane [6]. Equations 1 and 2 were found to be highly accurate over the reported range of measurements, even for this diversity of cases that typically span about 5 orders-of-magnitude in nucleation rate. Indeed a variety of techniques are available for homogeneous nucleation measurement, but each of these is typically limited in coverage to a range of 3 - 5 orders-of-magnitude in nucleation rate [See Fig. 1 of Ref. 7 for a comparison of various techniques and their range of rate coverage.] This is very encouraging: A good fit to multivariate nucleation data over the range of the aerosol chamber measurements (about 10^{-1} to $10^4 \text{ cm}^{-3} \text{ s}^{-1}$) is probably sufficient for most applications to atmospheric particle formation, and this now seems feasible using Eqs. 1 and 2 without significant higher order curvature corrections required.

As noted above, a local Arrhenius temperature dependence for the nucleation rate is expected from the second nucleation theorem. More surprising is the persistence of Arrhenius behavior over the full temperature range of the studied measurements. This is suggestive of a small difference in heat capacity between the critical cluster and its dissociated vapor form – the larger the difference in heat capacity, the greater the curvature expected in an Arrhenius plot. Related studies note a similar (linear in $1/T$) dependence, but for $\text{Log}(J/J_{CNT})$, where J_{CNT} is the classical nucleation rate, rather than for $\text{Log}J$ itself [5]. In a study of nucleation in condensed phase systems, the saturation pressure of water vapor over supercooled liquid at the homogeneous ice nucleation threshold, and at the efflorescence point for heterogeneous nucleation of ammonium sulfate onto small particles of calcium carbonate dispersed in a supersaturated aqueous solution of ammonium sulfate, were each found to follow the

Arrhenius temperature dependence. In these last two cases the measurements were of nucleation threshold conditions and not of nucleation rate [8].

Equations 1-3 are expressed in terms of vapor concentration, which is most useful for analysis of complex systems where even crude estimates of saturation vapor pressure are unavailable. Nevertheless, because saturation vapor pressures also tend to follow Arrhenius behavior, at least over short temperature spans, one can expect similar quality fits to experimental data with Eqs. 1-2 re-written in terms of $\ln S$ instead of $\ln n$. Thus comparable quality fits were obtained using the bi-linear form:

$$\ln J = a + b/T + c \ln S \quad (4)$$

to parameterize nucleation rates for the four unary vapor systems mentioned above. Equation 4 describes a plane in the 3D space of coordinates $\{\ln J, \ln S, 1/T\}$ and to a remarkable extent the experimental points were found to lie in this plane. Values for the quality of fit were obtained as: $R^2 = 0.94$ for water, 0.90 for nonane, 0.89 for methanol, and 0.97 for hexanol.

This paper examines this simple Arrhenius model, its connections to Hale's temperature dependent scaling of the nucleation rate [9], and comparisons between the two temperature functions. There are advantages and disadvantages to each approach: the Arrhenius model does an excellent job over temperature spans of at least 40K (the maximum range of the reported measurements). And because the Arrhenius model derives from the nucleation theorems, which are in turn based on the even more fundamental principles of mass action and detailed balance, the methods are not beholden to the usual drop-model assumptions of classical nucleation theory. The Hale scaling function, like the corresponding states temperature correlations that preceded it [10], find application over a much broader temperature range - but carry the disadvantage of being closely linked to the spherical drop model of classical nucleation theory.

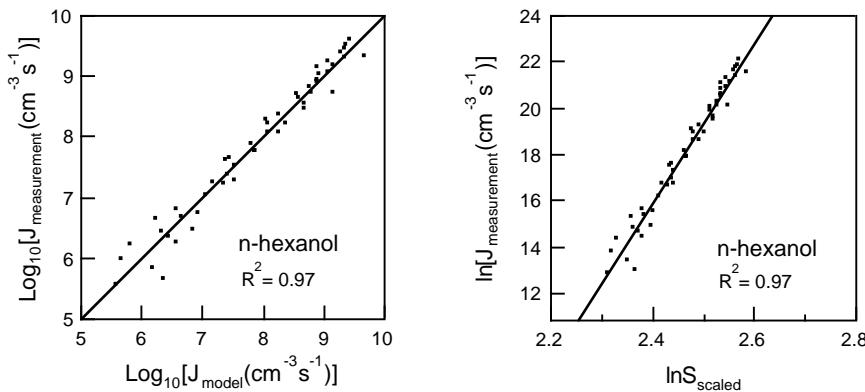


Figure 1. Comparison of measured n-hexanol nucleation rate with model predictions using the Arrhenius temperature dependence.

The Arrhenius scaling approach is illustrated here for n-hexanol vapor, the nucleation properties of which are known to depart strongly from the predictions of classical nucleation theory [5]. Figure 1 (left) illustrates the fit of the Arrhenius model

(Eq. 4) to the 50 hexanol measurements reported by Strey et al. (Fit parameters are: $a = 103.425$, $b = -47035.2$, $c = 34.6337$). The right panel of Fig. 1 shows the logarithm of the measured nucleation rate plotted versus the new Arrhenius-scaled supersaturation defined as:

$$\ln S_{scaled} = \ln S - \frac{E(g^*) - g^* E_1^b}{kg^*} \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (5)$$

where E_1^b is the energy per molecule in the *bulk liquid phase*. The slope of the regression line provides an estimate of the number of molecules of hexanol present in the critical nucleus, g^* . The numerator of the energy coefficient is the difference between the critical cluster energy and g^* molecules of the bulk phase. Its numerical value and g^* itself are each available from the fit parameters listed above in connection with Eq. 4. Thus $(E(g^*) - g^* E_1^b)/k = 47035 = -b$, a value grossly overestimated in predictions. based on the liquid drop model of classical nucleation theory. On the other hand the critical cluster size, $g^* = 34$ (to nearest integer), is in much closer agreement with $g_{CNT}^* = 36$ predicted by the Kelvin relation.

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